PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 04 April 2001 (04.04.01)	
International application No. PCT/US99/14393	**Applicant's or agent's file reference** AD6621
International filing date (day/month/year) 25 June 1999 (25.06.99)	**Priority date** (day/month/year)
Applicant PHILLIPS, Thomas, Richard	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

10 January 2001 (10.01.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Henrik Nyberg
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
AD6621		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 99/ 14393	25/06/1999	

Applicant

E.I. DU PONT DE NEMOURS AND COMPANY et al.

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [ ] the text is approved as submitted by the applicant.

   [X] the text has been established by this Authority to read as follows:

   COLORED POLYVINYL BUTYRAL INTERLAYER WITH IMPROVED HAZE PROPERTIES.

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. _____

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/14393

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B32B17/10 C08J3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 607 726 A (FLATTERY DAVID K ET AL) 4 March 1997 (1997-03-04) cited in the application claims 1-8	1,4
A	US 5 487 939 A (PHILLIPS THOMAS R ET AL) 30 January 1996 (1996-01-30) cited in the application claims 1-10	1,4
A	FR 2 080 154 A (GHARIANI LUCIEN) 12 November 1971 (1971-11-12) claims 1-6	1,4

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 February 2000	25/02/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Hallemeesch, A

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/14393

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 245 268 A (KEMISK VAERK KOGE A/S) 8 September 1971 (1971-09-08) claim 1 page 4, line 27 - line 41 examples 1-3,5	1,3
A	GB 2 122 364 A (CANON KK) 11 January 1984 (1984-01-11) claims 1,10 examples 1,3	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Info on patent family members

International Application No
PCT/US 99/14393

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5607726 A	04-03-1997	AT 174818 T	15-01-1999
		AU 698014 B	22-10-1998
		AU 3893395 A	06-05-1996
		BR 9509515 A	30-12-1997
		CZ 9701134 A	17-09-1997
		DE 69506902 D	04-02-1999
		DE 69506902 T	29-07-1999
		EP 0787043 A	06-08-1997
		ES 2127571 T	16-04-1999
		FI 971612 A	16-04-1997
		HU 77320 A	30-03-1998
		JP 10507405 T	21-07-1998
		NZ 295561 A	26-08-1998
		PL 319634 A	18-08-1997
		SI 9520098 A	31-12-1997
		SK 47497 A	10-09-1997
		WO 9611750 A	25-04-1996
US 5487939 A	30-01-1996	CA 2106212 A	15-09-1992
		WO 9216369 A	01-10-1992
		AU 662100 B	24-08-1995
		AU 7578891 A	21-10-1992
		BR 9107295 A	14-06-1994
		CS 9200761 A	16-09-1992
		DE 69126624 D	24-07-1997
		DE 69126624 T	08-01-1998
		EP 0576419 A	05-01-1994
		ES 2103808 T	01-10-1997
		JP 6507352 T	25-08-1994
		RU 2052301 C	20-01-1992
		MX 9201102 A	30-11-1992
FR 2080154 A	12-11-1971	NONE	
GB 1245268 A	08-09-1971	DK 145185 B	27-09-1982
		BE 720530 A	17-02-1969
		CH 520758 A	31-03-1972
		DE 1792462 A	22-04-1971
		FR 1581296 A	12-09-1969
		NL 6812555 A,B	10-03-1969
		SE 334963 B	10-05-1971
GB 2122364 A	11-01-1984	JP 1551099 C	23-03-1990
		JP 58200242 A	21-11-1983
		JP 62043173 B	11-09-1987
		DE 3318282 A	24-11-1983
		US 4980254 A	25-12-1990

PATENT COOPERATION TREATY

REC'D 08 OCT 2001

WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
AD6621		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US99/14393	25/06/1999	25/06/1999 None
International Patent Classification (IPC) or national classification and IPC B32B17/10		
Applicant E.I. DU PONT DE NEMOURS AND COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 9 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☒ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
10/01/2001	04.10.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Okunowski, J Telephone No. +49 89 2399 8975

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US99/14393

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-7 as originally filed

Claims, No.:

1-4 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

   ☐ restricted the claims.

   ☐ paid additional fees.

   ☐ paid additional fees under protest.

   ☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

   ☐ complied with.

   ☒ not complied with for the following reasons:
   see separate sheet

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

   ☒ all parts.

   ☐ the parts relating to claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 4
	No:	Claims 1-3
Inventive step (IS)	Yes:	Claims
	No:	Claims 4
Industrial applicability (IA)	Yes:	Claims 1-4
	No:	Claims

2. Citations and explanations
   see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Reference is made to the following documents:

D1: US-A-5 607 726
D2: US-A-5 487 939
D3: Kirk-Othmer Encyclopedia of Chemical Technology, 4th. ed., vol. 18 (1996); John Wiley & Sons, New York (US); p. 1059-1072
D4: Ullmann's Encyclopedia of Industrial Chemistry, 5th. ed., vol. A21 (1992); VCH Verlagsgesellschaft, D-6940 Weinheim; p. 750-752
D5: GB-A-1 245 268

The documents D3 and D4 were not cited in the international search report.

Item IV

This observation relates to claim 4 only. No objection under Rule 13.1 PCT is raised, provisionally, against the subject-matter of present claims 1-3.

Referring to the observations in Item V, point 1, first paragraph, below, the subject-matter of claim 4 (as far as it can be understood, see all of the clarity objections in Item VIII below) is, in one embodiment, a laminate which consists, in this order, of a glass layer, a polyvinyl butyral (PVB) sheeting, a coating of a blend of polyvinyl butyral and a pigment (colourant) which resides on the roughened surface of the PVB sheeting, and a glass layer. In a second, alternative embodiment, it is a laminate which consists, in this order, of a glass layer, a PVB sheeting comprising pigment (colourant), and another glass layer. As the first embodiment is not novel over D1 as well as over D2 (see Item V, point 1 below), there is not a single inventive concept which links the two alternatives of claim 4.

Claim 4 lacks therefore unity of invention, and is objectionable under Rule 13.1 PCT.

Item V

1 The glass laminate of claim 4 includes the process features of claim 1 only insofar as these process features are unambiguously discernable in the end product glass

laminate. Thus, in one embodiment, the subject-matter of claim 4 is a laminate which consists, in this order, of a glass layer, a polyvinyl butyral (PVB) sheeting, a coating of a blend of polyvinyl butyral and a pigment (colourant) which resides on the roughened surface of the PVB sheeting, and a glass layer. Attention is also drawn to the observations in points 2, 6 and 9 of Item VIII below, as to the non-distinguishing nature of several features in claim 1.

In D1, glass laminates with PVB sheeting interlayers are disclosed (column 2, line 66 to column 3, line 2; column 6, lines 43-49). Before incorporation between the glass layers, a coating is applied onto the roughened surface of the PVB sheeting (column 6, lines 28-42). The coating is a dried composition of PVB and a pigment (which conveys colour), see column 5, lines 21-65 of D1. An equivalent disclosure is found in D2 (column 2, lines 20-40; column 3, lines 57-66; column 4, lines 48- 65; column 5, lines 3-18).

Consequently, the subject-matter of present claim 4 lacks novelty over the disclosure of D1 as well as over the disclosure of D2 (Article 33(2) PCT).

2 Anyone of the disclosures of D1 and D2 can be seen as the closest prior art. The sole distinguishing feature of the subject-matter of present claim 1 is that the colour concentrate is present, at one stage of the process, in the form of solid chips. However, it is quite clear from the description that this feature is not at all instrumental in offering a solution to the actual problem addressed by the present application, i.e. the reduction of haze by pigment-coloured interlayers in glass laminates. The description makes quite clear that this is rather reached by low pigment particle size, which in turn is achieved by a particular combination of mixing apparatus, binder properties and blending/milling conditions. There is the additional advantage of ease of handling of chips, but this belongs to the basic knowledge in the field of dyeing.

As to the alternative of the direct melt-blending of the concentrate chips into the interlayer composition, this is a well-known alternative for the pigmenting of plastics (see D3, page 1069/1070: "**Plastics.**".
The subject-matter of claim 1, while being new, does therefore not involve an inventive step (Article 33(3) EPC).

3 The additional feature of present claim 2 is obvious as it is already suggested in D2, column 4, lines 48-65, where it is taught that haze is reduced upon pigment particle size reduction. In fact, it is not even a distinguishing feature, as D2 already uses pigment with a particle size optimised to minimalise haze, and as D1 uses exactly the same pigment as D2. Moreover, the particle sizes of present claim 2 are in fact the standard in the art (see D3, page 1059, first paragraph of "**Dispersion**".

The subject-matter of claim 2 does therefore not involve an inventive step (Article 33(3) EPC).

4 The additional feature of present claim 3 would still not limit the subject-matter of the claims to the essential features leading to minimal haze (see above). Moreover, an influence of the PVB binder molecular weight has only been shown with respect to PVB resin typically used to produce sheeting. However, it is known that high molecular weight PVB is suited for glass laminate interlayers, while lower molecular weight PVB is better for inks, pigment dispersions etc. (see D4, pages 751, 752). Interestingly, D5 already exemplified the use of Mowital[SPEC0416] B30 as binder.

The subject-matter of claim 3 does therefore not involve an inventive step (Article 33(3) EPC).

In fact, there does not seem to be a surprising teaching in the present application. Two-roll mills are known to produce high-quality pigment dispersions in thermoplastic resins (see D3, page 1062, last paragraph). Moreover, it is noted that the chip preparation according to the present application in the examples is done commercially (the ink preparation itself being according to D1 and D2), while this is not the case for the comparative examples. Thus, it seems that all someone skilled in the art would need to do to arrive at the present subject-matter is to do what he would do in practice anyway.

Item VII

1 The unit "centipoise" is no S.I.-unit of viscosity (Rule 10.1(e) PCT).

Item VIII

The claims lack clarity (Article 6 PCT)

1 The process of claim 1 is stated by claim 1 (first and second line) to be "A process for preparing colored thermoplastic composite sheeting for use in laminated structures". This implies that this process only relates to the preparation of a sheeting, not of a laminated structure. Yet, the last feature of claim 1 is the lamination of the sheeting between the surfaces of two layers of glass, i.e. the preparation of a laminated structure.

2 The term "low molecular weight" in claim 1 does not unambiguously delimit the molecular weight (and is therefore not distinguishing). Thus, claims 1, 2, 4 lack clarity.

3 The word "about" when used in connection with the definition with a range in claims 1 (10 to 60 weight percent) and 2 (50 to 500 nanometers), and in the corresponding parts of the description, detracts from the clarity of the claims.

4 It is not clear what is meant with "or directly melt incorporating" in claim 1. For instance, it is not clear into what the colour concentrate is to be incorporated.

5 In claim 1, it is not clear whether the chips comprise pigment and low molecular weight (?) polyvinyl butyral resin (PVB), or the chips comprise pigment and are themselves dispersed in PVB.

6 The definition of the pigment particle size in claim 1 is a definition of the pigment particle size by the desired result haze. Attention is drawn to page 3, lines 4 and 5 of the description, and PCT-Guidelines III-4.2. Moreover, the pigment particle size itself is also a desired result of the process of claim 1, which in fact relates, inter alia, to a way to obtain the particle size of claim 2 (see page 3, lines 6-11 of the description).

Also, the definition of the preselected pigment particle size by the effect of minimized haze lacks clarity because the term "minimize haze" does not unambiguously define

the extent of haze that would still be acceptable.

As a result, the definition of the particle size in claim 1 cannot be considered to be distinguishing.

7 Expressions in the description like "hereby incorporated by reference" effectively put the description into contradiction with the claims as concerns the exact scope of the claims, and thus detract from the clarity of the claims.

8 According to claim 1, the colour concentrate can be a dried coloured coating, i.e. it has been in solution before. However, it comprises, also according to claim 1, chips, and is therefore a particulate composition. This is contradictory.

9 According to claim 1, the colour concentrate consists for 10-60 wt% of the pigmented chips. However, according to the description (see e.g. Example 2), the colour concentrate which is used in directly melt incorporating consists for 100% of pigmented chips. Moreover, it is not clear whether this requirement is to apply to the colour concentrate in solid form, or to the solution of colour concentrate.

As a result, this feature cannot be considered to be distinguishing.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 January 2001 (04.01.2001)

PCT

(10) International Publication Number
WO 01/00404 A1

(51) International Patent Classification[7]: B32B 17/10, C08J 3/22

(21) International Application Number: PCT/US99/14393

(22) International Filing Date: 25 June 1999 (25.06.1999)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant *(for all designated States except US)*: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **PHILLIPS, Thomas, Richard** [US/US]; 5114 Glenbrook Drive, Vienna, WV 26105 (US).

(74) Agent: **DOBSON, Kevin, S.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States *(national)*: AE, AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/00404 A1

(54) Title: COLORED POLYVINYL BUTYRAL INTERLAYER WITH IMPROVED HAZE PROPERTIES

(57) Abstract: A laminar structure comprised of at least two layers of glass and a sheet of plasticized PVB prepared by providing a color concentrate comprised of solid pigmented chips wherein the chips have a preselected size range to minimize haze in the laminated structure and are dispersed in a low molecular weight polyvinyl butyral resin, said chips comprising from about 10 to 60 weight percent of the color concentrate, depositing said color concentrate on a roughened surface of polyvinyl butyral sheeting as a dried colored coating or directly melt incorporating, and thereafter laminating said sheeting between the surfaces of layers of glass.

INTERNATIONAL SEARCH REPORT

Inter Application No
PCT/US 99/14393

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B32B17/10 C08J3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 607 726 A (FLATTERY DAVID K ET AL) 4 March 1997 (1997-03-04) cited in the application claims 1-8	1,4
A	US 5 487 939 A (PHILLIPS THOMAS R ET AL) 30 January 1996 (1996-01-30) cited in the application claims 1-10	1,4
A	FR 2 080 154 A (GHARIANI LUCIEN) 12 November 1971 (1971-11-12) claims 1-6	1,4

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 February 2000	25/02/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hallemeesch, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter[redacted]Application No
PCT/US 99/14393

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 245 268 A (KEMISK VAERK KOGE A/S) 8 September 1971 (1971-09-08) claim 1 page 4, line 27 - line 41 examples 1-3,5	1,3
A	GB 2 122 364 A (CANON KK) 11 January 1984 (1984-01-11) claims 1,10 examples 1,3	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Application No
PCT/US 99/14393

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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

DOBSON, Kevin S.
E.I. DUPONT DE NEMOURS AND COMPANY
Legal Patent Records Center
1007 Market Street
Wilmington, Delaware 19805
ETATS-UNIS D'AMERIQUE

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	04.10.2001
Applicant's or agent's file reference: AD6621	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US99/14393	25/06/1999	25/06/1999

Applicant
E.I. DU PONT DE NEMOURS AND COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Ferro Vasconcelos, M Tel. +49 89 2399 ~~7595~~ 8052

REY NOTED

Form PCT/IPEA/416 (July 1992)

25 DE 2001

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
AD6621		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US99/14393	25/06/1999	25/06/1999
International Patent Classification (IPC) or national classification and IPC B32B17/10		
Applicant E.I. DU PONT DE NEMOURS AND COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 9 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☒ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
10/01/2001	04.10.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Okunowski, J Telephone No. +49 89 2399 8975

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US99/14393

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-7	as originally filed

Claims, No.:

1-4	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:
   - ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

☐ restricted the claims.

☐ paid additional fees.

☐ paid additional fees under protest.

☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

☐ complied with.

☒ not complied with for the following reasons:
see separate sheet

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

☒ all parts.

☐ the parts relating to claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 4
	No:	Claims 1-3
Inventive step (IS)	Yes:	Claims
	No:	Claims 4
Industrial applicability (IA)	Yes:	Claims 1-4
	No:	Claims

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Reference is made to the following documents:

D1: US-A-5 607 726
D2: US-A-5 487 939
D3: Kirk-Othmer Encyclopedia of Chemical Technology, 4th. ed., vol. 18 (1996); John Wiley & Sons, New York (US); p. 1059-1072
D4: Ullmann's Encyclopedia of Industrial Chemistry, 5th. ed., vol. A21 (1992); VCH Verlagsgesellschaft, D-6940 Weinheim; p. 750-752
D5: GB-A-1 245 268

The documents D3 and D4 were not cited in the international search report.

Item IV

This observation relates to claim 4 only. No objection under Rule 13.1 PCT is raised, provisionally, against the subject-matter of present claims 1-3.

Referring to the observations in Item V, point 1, first paragraph, below, the subject-matter of claim 4 (as far as it can be understood, see all of the clarity objections in Item VIII below) is, in one embodiment, a laminate which consists, in this order, of a glass layer, a polyvinyl butyral (PVB) sheeting, a coating of a blend of polyvinyl butyral and a pigment (colourant) which resides on the roughened surface of the PVB sheeting, and a glass layer. In a second, alternative embodiment, it is a laminate which consists, in this order, of a glass layer, a PVB sheeting comprising pigment (colourant), and another glass layer. As the first embodiment is not novel over D1 as well as over D2 (see Item V, point 1 below), there is not a single inventive concept which links the two alternatives of claim 4.

Claim 4 lacks therefore unity of invention, and is objectionable under Rule 13.1 PCT.

Item V

1 The glass laminate of claim 4 includes the process features of claim 1 only insofar as these process features are unambiguously discernable in the end product glass

laminate. Thus, in one embodiment, the subject-matter of claim 4 is a laminate which consists, in this order, of a glass layer, a polyvinyl butyral (PVB) sheeting, a coating of a blend of polyvinyl butyral and a pigment (colourant) which resides on the roughened surface of the PVB sheeting, and a glass layer. Attention is also drawn to the observations in points 2, 6 and 9 of Item VIII below, as to the non-distinguishing nature of several features in claim 1.

In D1, glass laminates with PVB sheeting interlayers are disclosed (column 2, line 66 to column 3, line 2; column 6, lines 43-49). Before incorporation between the glass layers, a coating is applied onto the roughened surface of the PVB sheeting (column 6, lines 28-42). The coating is a dried composition of PVB and a pigment (which conveys colour), see column 5, lines 21-65 of D1. An equivalent disclosure is found in D2 (column 2, lines 20-40; column 3, lines 57-66; column 4, lines 48- 65; column 5, lines 3-18).

Consequently, the subject-matter of present claim 4 lacks novelty over the disclosure of D1 as well as over the disclosure of D2 (Article 33(2) PCT).

2 Anyone of the disclosures of D1 and D2 can be seen as the closest prior art. The sole distinguishing feature of the subject-matter of present claim 1 is that the colour concentrate is present, at one stage of the process, in the form of solid chips. However, it is quite clear from the description that this feature is not at all instrumental in offering a solution to the actual problem addressed by the present application, i.e. the reduction of haze by pigment-coloured interlayers in glass laminates. The description makes quite clear that this is rather reached by low pigment particle size, which in turn is achieved by a particular combination of mixing apparatus, binder properties and blending/milling conditions. There is the additional advantage of ease of handling of chips, but this belongs to the basic knowledge in the field of dyeing.

As to the alternative of the direct melt-blending of the concentrate chips into the interlayer composition, this is a well-known alternative for the pigmenting of plastics (see D3, page 1069/1070: "**Plastics.**".
The subject-matter of claim 1, while being new, does therefore not involve an inventive step (Article 33(3) EPC).

3 The additional feature of present claim 2 is obvious as it is already suggested in D2, column 4, lines 48-65, where it is taught that haze is reduced upon pigment particle size reduction. In fact, it is not even a distinguishing feature, as D2 already uses pigment with a particle size optimised to minimalise haze, and as D1 uses exactly the same pigment as D2. Moreover, the particle sizes of present claim 2 are in fact the standard in the art (see D3, page 1059, first paragraph of "**Dispersion**".

The subject-matter of claim 2 does therefore not involve an inventive step (Article 33(3) EPC).

4 The additional feature of present claim 3 would still not limit the subject-matter of the claims to the essential features leading to minimal haze (see above). Moreover, an influence of the PVB binder molecular weight has only been shown with respect to PVB resin typically used to produce sheeting. However, it is known that high molecular weight PVB is suited for glass laminate interlayers, while lower molecular weight PVB is better for inks, pigment dispersions etc. (see D4, pages 751, 752). Interestingly, D5 already exemplified the use of Mowital[SPEC0416] B30 as binder.

The subject-matter of claim 3 does therefore not involve an inventive step (Article 33(3) EPC).

In fact, there does not seem to be a surprising teaching in the present application. Two-roll mills are known to produce high-quality pigment dispersions in thermoplastic resins (see D3, page 1062, last paragraph). Moreover, it is noted that the chip preparation according to the present application in the examples is done commercially (the ink preparation itself being according to D1 and D2), while this is not the case for the comparative examples. Thus, it seems that all someone skilled in the art would need to do to arrive at the present subject-matter is to do what he would do in practice anyway.

Item VII

1 The unit "centipoise" is no S.I.-unit of viscosity (Rule 10.1(e) PCT).

Item VIII

The claims lack clarity (Article 6 PCT)

1 The process of claim 1 is stated by claim 1 (first and second line) to be "A process for preparing colored thermoplastic composite sheeting for use in laminated structures". This implies that this process only relates to the preparation of a sheeting, not of a laminated structure. Yet, the last feature of claim 1 is the lamination of the sheeting between the surfaces of two layers of glass, i.e. the preparation of a laminated structure.

2 The term "low molecular weight" in claim 1 does not unambiguously delimit the molecular weight (and is therefore not distinguishing). Thus, claims 1, 2, 4 lack clarity.

3 The word "about" when used in connection with the definition with a range in claims 1 (10 to 60 weight percent) and 2 (50 to 500 nanometers), and in the corresponding parts of the description, detracts from the clarity of the claims.

4 It is not clear what is meant with "or directly melt incorporating" in claim 1. For instance, it is not clear into what the colour concentrate is to be incorporated.

5 In claim 1, it is not clear whether the chips comprise pigment and low molecular weight (?) polyvinyl butyral resin (PVB), or the chips comprise pigment and are themselves dispersed in PVB.

6 The definition of the pigment particle size in claim 1 is a definition of the pigment particle size by the desired result haze. Attention is drawn to page 3, lines 4 and 5 of the description, and PCT-Guidelines III-4.2. Moreover, the pigment particle size itself is also a desired result of the process of claim 1, which in fact relates, inter alia, to a way to obtain the particle size of claim 2 (see page 3, lines 6-11 of the description).

Also, the definition of the preselected pigment particle size by the effect of minimized haze lacks clarity because the term "minimize haze" does not unambiguously define

the extent of haze that would still be acceptable.

As a result, the definition of the particle size in claim 1 cannot be considered to be distinguishing.

7 Expressions in the description like "hereby incorporated by reference" effectively put the description into contradiction with the claims as concerns the exact scope of the claims, and thus detract from the clarity of the claims.

8 According to claim 1, the colour concentrate can be a dried coloured coating, i.e. it has been in solution before. However, it comprises, also according to claim 1, chips, and is therefore a particulate composition. This is contradictory.

9 According to claim 1, the colour concentrate consists for 10-60 wt% of the pigmented chips. However, according to the description (see e.g. Example 2), the colour concentrate which is used in directly melt incorporating consists for 100% of pigmented chips. Moreover, it is not clear whether this requirement is to apply to the colour concentrate in solid form, or to the solution of colour concentrate.

As a result, this feature cannot be considered to be distinguishing.

(19) RÉPUBLIQUE FRANÇAISE

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DE LA PROPRIÉTÉ INDUSTRIELLE

PARIS

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(15) BREVET D'INVENTION

PREMIÈRE ET UNIQUE PUBLICATION

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(51) Classification internationale (Int. Cl.).. **C 03 c 27/00//B 44 f 1/00.**

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(54) **Vitrages ou articles analogues à effets décoratifs.**

(72) Invention de :

(33) (32) (31) Priorité conventionnelle :

La présente invention se réfère aux vitrages, panneaux ou articles analogues constitués de feuilles superposées de verre collées entre elles au moyen d'une feuille intercalaire de matière thermoplastique.

Elle a pour objet un procédé qui consiste, dans le but d'obtenir des effets artistiques ou décoratifs, à peindre la feuille intercalaire avant de réaliser le collage des feuilles de verre.

L'invention permet d'obtenir des vitrages ou analogues présentant des motifs décoratifs et qui peuvent avantageusement remplacer les vitraux. De tels vitrages peuvent être particulièrement lumineux et la très grande gamme de couleurs utilisable permet toutes combinaisons d'effets ou de dessins désirées. Comme, d'autre part, il s'agit de produits feuilletés constitués de feuilles de verre assemblées par une matière plastique qui renforce considérablement lesdites feuilles, les articles obtenus peuvent être mis en place comme des vitrages de sécurité sans qu'il soit nécessaire de prévoir un encadrement de bois ou de métal. De même on peut donner aux vitrages de grandes dimensions sans utiliser de plombs ou de ferraillages comme dans les vitraux conventionnels. Par ailleurs ces vitrages présentent la caractéristique d'être "de sécurité" puisqu'en cas de casse la feuille intercalaire de matière plastique permet de maintenir en place les morceaux de verre cassé.

Suivant une autre caractéristique de l'invention, on utilise, pour peindre la feuille intercalaire de matière thermoplastique, des peintures dont les pigments sont dilués dans un agent constitué par une dissolution de la même matière thermoplastique que ladite feuille ou d'une matière thermoplastique différente mais dont la propriété est toujours de permettre le collage.

Si la feuille intercalaire est constituée en polyvinyl butyral, on utilisera avantageusement des peintures comportant elles-mêmes comme médium une dissolution de polyvinyl butyral dans de l'alcool isopropylique, la teneur en alcool isopropylique étant déterminée pour obtenir le degré de plasticité voulu par le peintre.

Les peintures peuvent être appliquées par tout procédé approprié, par exemple au pinceau, au couteau, à la racle, au pistolet, etc...

Ces peintures peuvent comporter des constituants auxiliaires tels que des retardateurs.

Les couches colorées peuvent comprendre des éléments tels que des feuilles très minces ou des particules, constituées par exemple par des métaux ou des oxydes métalliques de couleurs diverses, la combinaison de ces éléments avec les couches colorées pouvant conduire à l'obtention d'effets décoratifs particulièrement intéressants.

On peut également utiliser plusieurs feuilles intercalaires de matière thermoplastique diversement colorées, ce qui permet d'obtenir des effets lumineux de profondeur particulièrement intéressants.

On donne ci-après un exemple de fabrication de vitrages feuilletés suivant l'invention constitués de deux feuilles de verre avec feuille intercalaire en polyvinyl butyral.

La feuille intercalaire est colorée, suivant le dessin voulu, avec les peintures ci-dessus dont les pigments sont dilués dans une dissolution de polyvinyl butyral dans de l'alcool isopropylique. Cette feuille est ensuite séchée dans une enceinte à 15°C et 20 % d'humidité.

La première feuille de verre, préalablement lavée et séchée, est posée à plat sur une table, On la recouvre de la feuille de matière plastique et on met ensuite en place la deuxième feuille de verre, également lavée et séchée, sur la feuille intercalaire.

Cet ensemble, préalablement chauffé à environ 60°C, est calandré dans une presse à rouleaux, ce qui permet d'évacuer la totalité de l'air inclus entre les deux feuilles de verre et la feuille de matière plastique. Ce chauffage permet également d'effectuer un pré-collage des trois éléments.

L'ensemble ainsi pré-collé est ensuite introduit dans un autoclave relié à une source d'air sous pression et équipé de résistances électriques. La température et la pression de l'air sont graduellement portées à environ 120 à 130°C et à 12 kg/cm^2. Cette étape opératoire dure à peu près une heure et en maintenant la pression à 12 kg/cm^2 en supprimant l'alimentation des résistances, on refroidit l'autoclave jusqu'à arriver à la température ambiante.

Le vitrage ainsi obtenu est constitué par les deux feuilles de verre intimement soudées par la feuille de matière thermoplas-

tique. Celle-ci étant incolore, seule la peinture appliquée sur ladite feuille est visible.

Il doit être bien entendu que l'invention n'est pas limitée à cet exemple de réalisation. C'est ainsi que l'on peut réaliser des vitrages feuilletés comportant plus de deux feuilles de verre associées les unes aux autres par des feuilles de matière thermoplastique qui peuvent être peintes de diverses façons. De même les feuilles de verre peuvent être bombées ou de forme irrégulière. Dans ce cas, au lieu de calandrer l'ensemble des feuilles de verre avec la ou les feuilles de matière thermoplastique peintes, on le soumet d'abord à un traitement de dégazage sous vide à une température de 60°C puis on procède au traitement dans un autoclave sous la pression et à la température indiquées ci-dessus.

REVENDICATIONS

1) Procédé pour la fabrication de vitrages, panneaux ou analogues, constitués de feuilles superposées de verre collées entre elles au moyen d'une feuille intercalaire de matière thermoplastique, caractérisé en ce que, dans le but d'obtenir des effets décoratifs ou artistiques, ladite feuille de matière thermoplastique est peinte avant de procéder au collage des dites feuilles de verre.

2) Procédé suivant la revendication 1, caractérisé en ce que, pour peindre la feuille intercalaire de matière thermoplastique, on utilise des peintures dont les pigments sont dilués dans un médium constitué par une dissolution de la même matière thermoplastique ou d'une matière thermoplastique différente permettant le collage des feuilles.

3) Procédé suivant les revendications 1 et 2, caractérisé en ce que l'on rapporte sur la feuille intercalaire des éléments, tels que des feuilles minces ou des particules de couleurs diverses constituées par exemple de métaux ou d'oxydes métalliques.

4) Procédé suivant les revendications 1 et 2, caractérisé en ce que la feuille intercalaire est constituée en polyvinyl butyral, les peintures comportant elles-mêmes comme médium une dissolution de polyvinyl butyral dans de l'alcool isopropylique.

5) Procédé suivant la revendication 4, caractérisé en ce que, après avoir formé l'empilage des feuilles de verre et de la feuille intercalaire entre chaque feuille de verre, l'ensemble est chauffé à une température d'environ 60°C, calandré pour obtenir un pré-collage, puis introduit dans un autoclave dans lequel la pression est portée graduellement à environ 12 kg/cm^2 et à la température d'environ 120-130°C pour achever le collage, l'ensemble étant ensuite refroidi lentement en maintenant la pression.

6) Vitrages, panneaux ou articles analogues, constitués de feuilles de verre superposées, collées entre elles au moyen d'une feuille intercalaire de matière thermoplastique, caractérisés en ce que la feuille intercalaire est colorée.

(12) UK Patent Application (19) GB (11) 2 122 364 A

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GB 1392929
GB 1362682
US 4308334
US 4242432
(58) Field of search
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(54) **Electrophotographic photosensitive member**

(57) An electrophotographic photosensitive member comprising a conductive substrate and a photosensitive layer or layers which contains pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number of the total pigment. The particles of the above-mentioned size distribution are dispersed in a binder.

GB 2 122 364 A

The Chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

SPECIFICATION

Electrophotographic photosensitive member

The present invention relates to an electrophotographic photosensitive member, and more particularly, to an electrophotographic photosensitive member having functionally specialized photosensitive layers comprising a charge generation layer forming an electric charge on exposure to light and a charge transport layer transporting the generated charge.

Inorganic photoconductive materials such as selenium, cadmium sulfide, zinc oxide and the like have been widely known heretofore.

On the other hand, various organic photoconductive polymers have been proposed such as polyvinyl carbazole and the like. Such polymers have indeed satisfactory transparency, film-forming property and flexibility. Nevertheless, those polymers have not been commercialized until now because they are inferior to inorganic photoconductive materials in photosensitivity, durability, and stability to the variation of the environment. A photosensitive member prepared from an organic photoconductive material of low molecular weight combined with a binder has also been proposed, but it does not have sufficient photosensitivity yet.

In order to remove such drawbacks, a laminated structure has been proposed lately wherein the photosensitive layer is functionally divided into two layers of a charge generating layer and a charge transport layer, for example, in the diclosure in the United States Patens No. 3,837,851 and No. 3,871,882. The sensitivity of the photosensitive layer having such laminated structure is known to be affected by the thickness ratio of the charge generation layer to the charge transport layer, as is disclosed in Australian Laid-open Patent Specification No. 87757/75.

The inventors, after a lot of study, have found that the size distribution of the pigment used in the charge generation layer has a great influence on the photosensitivity, and have accomplished the present invention.

According to one aspect of the present invention, there is provided an electrophotographic photosensitive member having an electroconductive substrate and a photosensitive layer or layers, characterized in that the photosensitive layer or layers contains pigment articles of 0.5 μ or below in size in an amount of 80% or more in weight or number of the total pigment particles, and the particles of said size distribution are dispersed in a binder.

According to another aspect of the present invention, there is provided an electrophotographic process which comprises:

a) a step of charging an electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductive substrate, said charge generation layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin.
b) a step of exposing the charged electrophotographic photosensitive member.
c) a step of developing with a developer.

According to a further aspect of the present invention, there is provided an electrophotographic process which comprises carrying out the following steps a), b), c), d) and e) at least twice:

a) a step of charging an electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductive substrate, said charge generation layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,
b) a step of exposing the charged electrophotographic photosensitive member,
c) a step of developing using a developer,
d) a step of transferring the developed images onto a receiving member,
e) a step of cleaning the remainder developer.

According to a further aspect of the present invention, there is provided an electrophotographic process which comprises:

a) a step of charging an electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductive substrate, said charge generation layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,
b) a step of exposing the charged electrophotographic photosensitive member by laser beam scanning,
c) a step of developing with a developer.

According to a further aspect of the present invention, there is provided an electrophotographic process which comprises carrying out the following steps a), b), c), d) and e) at least twice:

a) a step of charging an electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductiv substrate, said charge generation layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin.
b) a step of exposing the charged electrophotographic photosensitive member with laser beam scanning,
c) a step of developing with a developer,
d) a step of transferring developed images onto a receiving member,

e) a step of cleaning the remaining developer.

According to a further aspect of the present invention, there is provided an electrophotographic process which comprises:

a) a step of charging an electrophotographic photosensitive member having a photosensitive layer or layers on an electroconductive substrate, said photosensitive layer comprising pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin.

b) a step of exposing the charged electrophotographic photosensitive member,

c) a step of developing with a developer.

According to a further aspect of the present invention, there is provided an electrophotographic process which comprises carrying out the following steps a), b), c), d) and e) at least twice:

a) a step of charging an electrophotographic photosensitive member having a photosensitive layer or layers on an electroconductive substrate, said photosensitive layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,

b) a step of exposing the charged electrophotographic photosensitive member,

c) a step of developing with a developer,

d) a step of transferring the developed images onto a receiving member,

e) a step of cleaning the remaining developer.

In an electrophotographic photosensitive member of a laminated structure comprising a conductive substrate, a charge generation layer and a charge transport layer laminated in this order, the preferred embodiment of the present invention uses the charge generating pigment of such a particle size distribution that the particles of 0.5 μ or below, preferably 0.3 μ or below, especially preferably 0.1 μ or below, or the most preferably 0.01 μ or below in size account for 80% or more in weight or number of the total pigment, and the pigment particles are dispersed in a binder, serving as a charge generation layer.

In another embodiment of the present invention, there may be used the pigment particles having such a narrow size distribution that the particles of the size of 0.02 μ - 0.5 μ, especially preferably 0.02 μ - 0.3 μ, account for more than 80% in weight or number of the total pigment.

The charge generating layer of the present invention is formed by coating the binder dispersion of the charge generating pigment particles of the above-mentioned particle size distribution onto the electroconductive substrate by various coating methods such as dip coating, spray coating, spinner coating, bead coating, Meyer bar coating, blade coating, roller coating, curtain coating, and the like, and then drying it. The thickness of the charge generation layer is preferably 0.01 μ - 1 μ, and the smaller thickness causes the lower sensitivity. The larger thickness lowers a charging potential, leading to an increased optical memory.

The weight ratio of the charge generating pigment to the binder is usually in the range of from about 5 : 1 to 1 : 5, preferably from about 2 : 1 to 1 : 4.

The preparation of the dispersion in the present invention is carried out generally by mixing and dispersing the pigment with an organic binder resin using a sand mill or a ball mill, but the pigment in a dry state, such as in crystal or powder state may be separately and preliminarily pulverized to obtain the required particle size distribution using a commercially available pulverizer such as a ball mill, a jet mill and the like, and then may be dispersed in a binder.

Otherwise, the pigment in a slurry or suspension state may be pulverized by means of a sand mill or a ball mill to obtain the required particle size distribution and then may be dispersed in the binder. The method for preparing the binder dispersion is not limited to the above-described one, but any method may be used as far as a binder dispersion of the pigment particles of the above-mentioned particle size distribution can be obtained.

Various filters, such as "Membrane Filter" supplied by Toyo Kagaku Sangyo K.K., may be used for preparing the pigment particles of the above-mentioned particle size distribution.

The particle size distribution may be measured by means of Horiba centrifugal automatic particle size distribution measuring apparatus made by Horiba, Ltd. This apparatus measures the changes of absorbance per unit time to give particle size distributions. The dependence of time of sedimentation on particle diameters is represented by Stokes' equation (1) shown below, which is derived from the phenomina that particles of larger size settle faster than smaller ones. For centrifugal sedimentation

$$D = \left[\frac{18\,\eta_o\,\ell n\,(X_2/X_1)}{(\rho - \rho_o)\,\omega^2 t}\right]^{1/2} \quad \ldots\ldots (1)$$

where D : particle size (cm)
η_o : viscosity coefficient of solvent
H : distance of settling (cm)
ρ : density of sample (g/cm^3)
ρ_o : density of solvent (g/cm^3)
t : time of sedimentation (sec)
X_1 : distance from the center of rotation to the plane of sedimentation (cm)
X_2 : distance from the center of rotation to the plane of measurement (cm)
ω : angular velocity (rad/sec)
g : gravitational acceleration (cm/s^2)

On the other hand, formula (2) are known to hold between settling particles and light absorbance.

$$\ell n\, Io - \ell n\, Ii = K \sum_{i=1}^{n} NiDi^2 \quad \ldots\ldots (2)$$

where
Io : quantity of transmitted light through solvent
Ii : quantity of transmitted light in the presence of particles Di
K : constant
Ni : numbers of particles Di
Di : diameter of the i-th particle

($NiDi^2$) in formula (2) is based on area, and by multiplying formula (2) by Di the base is converted to volume. Therefore, the measurement of the change of the concentration (absorbance) of a pigment dispersion can give a particle size distribution.

As the examples of the charge generating substances, there may be mentioned photoconductive substances as shown below: azo pigments (disazo pigments and trisazo pigments) such as Sudan Red, Diane Blue, and Janus Green B; quinone pigments such as Algol Yellow, Pyrene Quinone, and Indanthrene Brilliant Violet RRP; chinocyanine pigments, pyrene pigments, indigo pigments such as indigo, thioindigo and the like; bisbenzimidazole pigments such as Indofast Orange toner and the like; phthalocyanine pigments such as copper phthalocyanine and the like; quinacridone pigments, and the like.

Among various binders, organic binder resins are especially suitable for the present invention, and there may be used preferably polyester, polystyrene, polyvinyl chloride, polyvinyl acetate, acrylic resins, polyvinylpyrrolidone, methylcellulose, hydroxypropyl methylcellulose, polyvinylbutryal, cellulose acetate butyrate and the like.

As a solvent for preparing the dispersion, there may be used methyl ethyl ketone, cyclohexanone, ethyl acetate, water and the like which easily dissolve the organic binder resin.

As an electroconductive substrate in the present invention which is coated with the charge generating layer, there may be used electroconductive materials such as aluminum, aluminum alloy, copper and the like, plastics having vacuum-deposited metal layer, a substrate consisting of plastics coated by electroconductive particles along with a suitable binder, a substrate obtained from plastics or paper having electroconductive particles immersed or dispersed into it, and plastics containing electroconductive polymer.

Undercoat having barrier and adhesion function may be provided between the electroconductive substrate and the charge generating layer. The undercoat may be formed of casein, polyvinyl alcohol, polyamide or the like, and the thickness of the film is usually 0.1 μ - 5 μ, preferably 0.5 μ - 3 μ.

The charge transport layer overlying the charge generating layer is formed by blending a film-forming resin with a charge transporting compound that has a radical or radicals of polynuclear aromatic compounds such as anthracenes, pyrenes, phenanthrenes, coronenes, and the like in the main chain or the side chain, or nitrogen-containing heterocyclic compounds such as indoles, carbazoles, oxazoles, isoxazoles thiazoles, imidazoles, pyrazoles, oxadiazoles, pyrazolines, thiaziazoles, triazoles, and the like in the main chain or the side chain, or hydrazones. This is because such charge transporting substances are generally low molecular weight compounds and hav poor film-forming ability. As such resins, there may be used polyesters, polysulfones, polycarbonates, polymethacrylates, polystyrenes, and the like.

The charge transport layer is preferably 5 μ - 20 μ in thickness, and may contain various additives such as diphenyl, o-terphenyl, p-terphenyl, dibutyl phthalate, dimethylglycol phthalate, dioctyl phthalate, triphenyl phosphoric acid, methylnaphthalene, benzophenone, chlorinated paraffines, dilauryl thiopropionate,

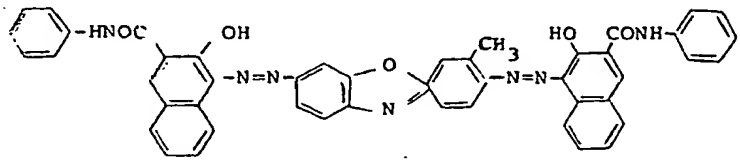
3,5-dinitrosalicylic acid, and various fluorocarbons.

The electrophotographic photosensitive member of the present invention may be used not only for electrophotographic copiers but also used in the application fields of electrophotography such laser printer using argon gas laser, helium-neon gas laser, or semiconductor laser, CRT printer and electrophotographic plate making systems.

The following examples will illustrate the present invention.

Example 1

As a charge generating material, there was used a disazo pigment of the structural formula:



and as an organic binder resin there was used polyvinyl butryal resin (Trade Name Eslec BM-2, made by Sekisui Chemical Co., Ltd.).

3 g of the above-mentioned diazo pigment was added to the resin solution made by dissolving 1.5 g of polyvinylbutyral resin in 50 g of cyclohexanone and was dispersed by means of a sand mill to prepare the dispersion of charge generating pigment particles in an organic binder resin. The particle distribution of the dispersion was measured by the particle size distribution measuring apparatus (CAPA-500, made by Horiba, Ltd.). At the same time, there was used a reference samples in which the pigment is removed from the test samples. In the examples hereinafter, the particle distribution were measured in the same manner as in this example.

The Table 1 shows the condition of dispersing and the resulting particle size distribution.

TABLE 1

Sample No.	Time of dispersion (Hours)	Particle size distribution (weight %) less than 0.02μ	0.02~0.06μ	0.06~0.1μ	0.1~0.3μ	0.3~0.5μ	0.5~1μ	more than 1μ
1-1	0.25	-	-	6.2	23.7	30.2	34.7	5.2
1-2	1	2.4	9.2	28.4	31.8	22.4	4.6	1.2
1-3	5	14.0	37.7	25.5	14.6	7.6	0.6	-
1-4	10	39.0	31.9	17.1	8.1	3.7	0.2	-
1-5	20	59.2	22.7	10.3	5.2	2.6	-	-
1-6	40	68.4	19.5	8.4	2.9	0.8	-	-

The figures in the Table are the ones that are obtained by converting the measured volume-based percentage into weight percentage.

The above-mentioned dispersion was applied onto the aluminum cylinder of 80 mmø × 300 mm undercoated with casein of 3 μ thick, by dip coating, and dried at 100°C for 10 minutes to form a charge generating layer of 0.8 μ thick.

Then 10 parts of 1-[pyridyl-(2)]-3-(4-N,N-diethylaminostyryl)-5-(4-N,N-diethylaminophenyl) pyrazoline, and 10 parts of polysulfone resin (Trade Name: U-Del P-1700, made by UCC) was dissolved in 80 parts of monochlorobenzene, and the solution was applied onto the charge generation layer by dip coating, and was dried with hot air at 100°C to form a charge transport layer of 12 μ thick.

The electrophotographic photosensitive member thus prepared was set on an electrophotographic copier having steps of corona charging of −5.6 KV, image forming, light exposure, dry development using dry toner developer, toner transfer to plain paper (a receiving member), and cleaning by urethane rubber blade. The sensitivity (expressed by the quantity of exposure light necessary to reduce the surface potential of a photosensitive member to half value) was determined. Table 2 shows the results.

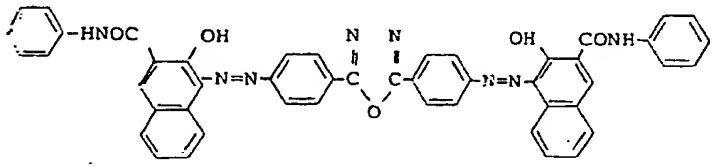
The sensitivity was largely dependent on the particle size distribution of the charge generating substances, and the samples of Nos. 2 - 6 of the present invention had high sensitivities.

TABLE 2

Photo-sensitive member No.	Charge generating pigment dispersion No.	Surface potential (volts)	Sensitivity (lux.sec.)
1	1-1	−550	13.0
2	1-2	−560	10.5
3	1-3	−565	6.4
4	1-4	−560	5.4
5	1-5	−540	5.5
6	1-6	−550	4.8

Example 2

As a charge generating material, a disazo pigment of the following structural formula was used:



and an alcohol-soluble phenolic resin (Trade Name: Plyophen 5010, supplied by Dai Nippon Ink and Chemicals Inc.) was used as the organic binder resin.

2.6 g of the above-mentioned alcohol-soluble phenolic resin (solid content: 58%) and 50 g of ethanol were mixed well, and the above-mentioned disazo pigment was added to the resulting mixture and dispersed by a sand mill to prepare an organic binder resin dispersion of charge generating pigment particles.

The above-mentioned dispersion was applied onto an aluminum cylinder of 80 mmø × 300 mm undercoated with casein of 3 μ thick by dip coating, and dried at 80°C for 5 minut s to form a charge generation layer of 0.9 μ thick.

Then, the same charge transport layer as in Example 1 was formed on the charge generation layer and the sensitivity of the electrophotographic photosensitive member thus obtained was measured in the same manner as in Example 1.

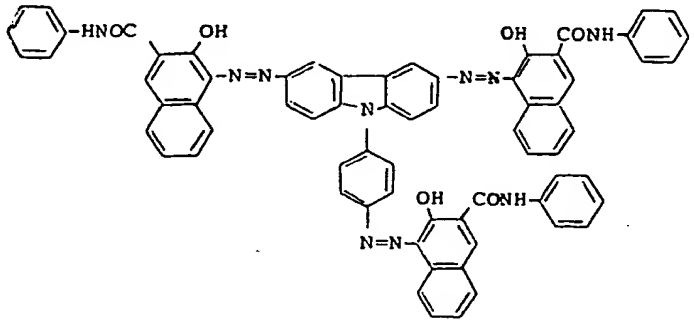
The results were shown in Table 3.

TABLE 3

Sample No.	Charge generating pigment dispersion Sample No.	Time of dispersion (Hours)	Particle size distribution (Weight %) less than 0.2μ	0.02~0.06μ	0.06~0.1μ	0.1~0.3μ	0.5~0.5μ	0.5~1μ	more than 1μ	Surface potential (V)	Sensitivity (lux.sec)
7	2-1	0.25	-	-	-	25.1	40.6	19.5	14.8	−545	16.5
8	2-2	10	28.6	45.0	18.6	4.6	2.6	0.6	-	−560	7.6
9	2-3	20	50.8	33.7	10.1	4.1	1.2	0.1	-	−550	5.9
10	2-4	40	71.3	18.7	5.9	3.2	0.9	-	-	−560	5.4

Example 3

A trisazo pigment of the structural formula as shown below was used as a charge generating material:



Polyvinylbutryal (trade name: Eslec BM-1, supplied by Sekisui Chemical Co., Ltd.) was used as a binder, and was dispersed by a sand mill using isopropyl alcohol as a solvent to obtain a dispersion of a charge generating pigment particles in an organic binder resin in the same manner as in Example 1.

The above-mentioned dispersion was applied onto an aluminum cylinder of 80 mmø × 300 mm undercoated with casein of 3 μ thick by dip coating, and dried at 80°C for 5 minutes to obtian a charge generation layer of 0.8 μ thick.

Then the same charge transport layer as in Example 1 was formed on the charge generation layer to prepare an electrophotographic photosensitive member. The photosensitive member thus obtained was set on the electrophotographic copier used in Example 1, and the light portion potential (V_L) and the dark portion potential (V_D) were measured. The sensitivity was measured in the same manner as in Example 1, wherein the quantity of exposure light was controlled so that the initial V_L of the photosensitive member of Sample No. 11 be −50V at the exposure.

The results are shown in Table 4.

TABLE 4

Photo sensitive member No.	Charge generating pigment dispersion No.	Time of dispersion (Hours)	Particle size distribution (Weight %) less than 0.02μ	0.02~0.06μ	0.06~0.1μ	0.1~0.3μ	0.3~0.5μ	0.5~1μ	more than 1μ	V_L (volts)	V_D (volts)	Sensitivity (lux.sec)
11	3-1	0.25	-	-	-	10.8	59.6	16.8	12.8	−50	−550	14.8
12	3-2	20	17.8	20.1	30.8	24.7	5.8	0.8	-	−60	−560	6.3
13	3-3	40	15.4	38.5	26.9	15.5	3.3	0.4	-	−50	−560	5.2

9

The photosensitive members of Sample Nos. 11 - 13 were set respectively on the electrophotographic copier used in Example 1, were repeatedly subjected to the electrophotographic process comprising charging, exposure, development, image transfer, cleaning, and discharge by exposure. When 10,000 copies were made, the light portion potential (V_L) and the dark portion potential (V_D) of each photosensitive member were measured in the same manner as in Example 1. The results were shown in Table 5.

TABLE 5

Photosensitive Member Sample No.	After 10,000 copies were made V_L (volts)	V_D (volts)	Sensitivity (lux-sec)
11	−70	−410	25.7
12	−80	−500	8.6
13	−70	−520	7.3

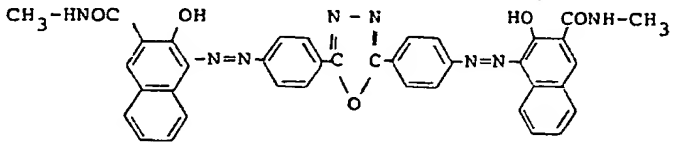
As Table 5 clearly shows, the photosensitive members including a charge generation layer prepared from the pigment particles of such a narrow particle size distribution that particles of 0.02 μ - 0.3 μ account for 80% or more in weight of the total pigment particles had stable charging characteristics and stable sensitivities even after repeated electrophotographic processings, compared with the comparative sample (No. 11) having the charge generation layer prepared from the pigment of a wide particle size distribution.

Especially according to Sample No. 13, the stabilities of the charging characteristics and the sensitivity were satisfactory when the pigment particles used had such narrow particle size distribution that more than 50 weight %, preferably more than 60 weight % of the particles was in the range of from 0.02 μ to 0.3 μ.

Examples 4 - 6

The experiments were carried out in the same manner as in Example 1, except that the charge generating materials, organic binder resins and solvents shown below were used. The particle size distribution of each charge generating material was such that the particles of 0.02 μ - 0.3 μ account for 96 weight % of the total particles.

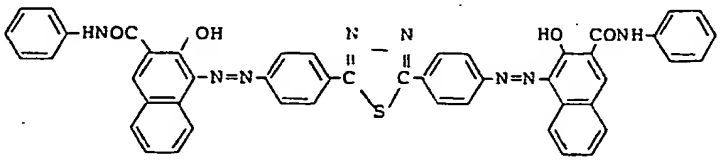
4. Charge generating substance:



Organic binder resin: polyvinylbutyral resin
(trade name: Eslec BXL, supplied by Sekisui Chemical Co., Ltd.)

Solvent: methyl ethyl ketone

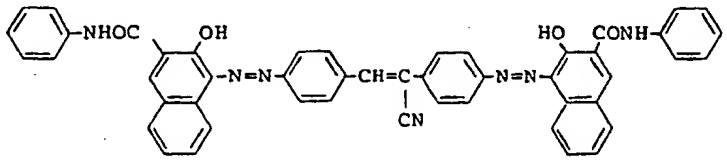
5. Charge generating substance:



Organic binder resin:
Cellulose acetate butyrate (trade name: CAB-381-0.5, supplied by Eastman Kodak Co.)

Solvent: cyclohexan ne

6. Charge generating substance:



Organic binder resin:
Cellulose acetate butyrate (trade name: CAB-381-0.5, supplied by Eastman Kodak Co.)

Solvent: cyclohexanone

The charging characteristics and the sensitivities were measured in the same manner as in Example 3, where the quantity of exposure light was controlled so that the initial V_L of the photosensitive member of Example 4 is −50V. The results were shown in Table 6.

TABLE 6

Example No.	Initial V_L (volts)	V_D (volts)	Sensitivity (lux-sec)	After 10,000 copies were made V_L (volts)	V_D (volts)	Sensitivity (lux-sec)
4	−50	−560	5.6	−60	−480	7.1
5	−50	−550	7.3	−70	−500	7.9
6	−50	−560	5.1	−60	−490	6.4

CLAIMS

1. An electrophotographic photosensitive member having an electroconductive substrate and a photosensitive layer or layers, characterized in that the photosensitive layer or layers contains pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number of the total pigment particles, and the particles of said size distribution are dispersed in a binder.

2. An electrophotographic photosensitive member according to Claim 1, wherein the photosensitive layer or layers has a laminated structure comprising a charge generation layer and a charge transport layer, said charge generation layer contains pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution are dispersed in an organic binder resin.

3. An electrophotographic photosensitive member according to Claim 2, wherein the charge generation layer contains pigment particles of 0.3 μ or below in size in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

4. An electrophotographic photosensitive member according to Claim 3, wherein the charge generation layer contains pigment particles of 0.1 μ or below in size in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

5. An electrophotographic photosensitive member according to Claim 4, wherein the charge generation layer contains pigment particles of 0.06 μ or below in size in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

6. An electrophotographic photosensitive member according to Claim 2, wherein the charge generation layer contains pigment particles ranging in size from 0.02 μ to 0.5 μ in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

7. An electrophotographic photosensitive member according to Claim 6, wherein the charge generation layer contains pigment particles ranging in size from 0.02 μ to 0.3 μ in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

8. An electrophotographic photosensitive member according to Claim 7, wherein the charge generation layer contains pigment particles ranging in size from 0.02 μ to 0.1 μ in an amount of 50% or more in w ight or number, and the particles of said size distribution are dispersed in an organic binder resin.

9. An electrophotographic photosensitive member according to Claim 8, wherein the charge generation layer comprises pigment particles ranging from 0.02 μ to 0.1 μ in an amount of 60% of more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

10. An electrophotographic photosensitive member according to any preceding claim wherein the pigment particles are particles of at least one pigment selected from disazo pigments, trisazo pigments, quinone pigments, chinocyanine pigments, perylene pigments, indigo pigments, bisbenzimidazole pigments, phthalocyanine pigments, and quinacridone pigments.

11. An electrophotographic photosensitive member according to Claim 10 wherein the pigment particles are disazo pigment particles or trisazo pigment particles.

12. An electrophotographic photosensitive member according to Claim 10 wherein the pigment particles are phthalocyanine pigment particles.

13. An electrophotographic photosensitive member according to Claim 12, wherein the pigment particles are copper phthalocyanine particles.

14. An electrophotographic photosensitive member according to Claim 2 or any of Claims 3 to 13 as dependent thereon, wherein the charge generation layer comprises pigment particles and an organic binder resin in the weight ratio of from 5:1 to 1:5.

15. An electrophotographic photosensitive member according to Claim 14, wherein the charge generation layer comprises pigment particles and an organic binder resin in the weight ratio of from 2:1 to 1:4.

16. An electrophotographic photosensitive member according to Claim 2 or any of Claims 3 to 15 as dependent thereon wherein the charge generation layer has a film thickness of from 0.01 to 1 μ.

17. An electrophotographic photosensitive member according to Claim 2 or any of Claims 3 to 16 as dependent thereon which has a photosensitive layer or layers of a laminated structure wherein a charge transport layer is laminated contiguously onto a charge generation layer.

18. An electrophotographic photosensitive member according to Claim 17, wherein the charge transport layer comprises at least one compound selected from polynuclear aromatic compounds, nitrogen-containing heterocyclic compounds and hydrazone compounds, and an organic binder resin.

19. An electrophotographic photosensitive member according to Claim 18, wherein the charge transport layer comprises hydrazone compound or compounds and an organic binder resin.

20. An electrophotographic photosensitive member according to Claim 18, wherein the charge transport layer comprises a pyrazoline compound or compounds and an organic binder resin.

21. An electrophotographic photosensitive member according to any of Claims 17 to 20 wherein an undercoat layer is present between the electroconductive substrate and the charge generation layer.

22. An electrophotographic photosensitive member according to Claim 21, wherein the undercoat layer is a film of casein, polyvinyl alcohol, or polyamide.

23. An electrophotographic photosensitive member according to Claim 22, wherein the undercoat layer is a film of polyamide.

24. An electrophotographic process which comprises:

a) a step of charging an electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductive substrate, said charge generation layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,

b) a step of exposing the charged electrophotographic photosensitive member,

c) a step of developing with a developer.

25. An electrophotographic process according to Claim 24, wherein the charge generation layer contains pigment particles ranging in size from 0.02 μ to 0.5 μ in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

26. An electrophotographic process which comprises carrying out the following steps a), b), c), d) and e) at least twice:

a) a step of charging an electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductive substrate, said charge generation layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,

b) a step of exposing the charged electrophotographic photosensitive member,

c) a step of developing using a developer,

d) a step of transferring the developed images onto a receiving member,

e) a step of cleaning the remaining developer.

27. An electrophotographic process according to Claim 26, wherein the charge generation layer contains pigment particles ranging in size from 0.02 μ to 0.5 μ in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

28. An electrophotographic process which comprises:

a) a step of charging an electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductive substrate, said charge generation layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,

b) a step of exposing the charged electrophotographic photosensitive member by laser beam scanning,

c) a st p of developing with a developer.

29. An electrophotographic process according to Claim 28, wherein the charge g neration layer contains pigment particles ranging in size from 0.02 μ to 0.5 μ in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

30. An electrophotographic process which comprises carrying out the following steps a), b), c), d) and e) at least twice:

a) a step of charging an electrophotographic photosensitive member having a charge generation layer and a charge transport layer on an electroconductive substrate, said charge generation layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,

b) a step of exposing the charged electrophotographic photosensitive member with laser beam scanning,

c) a step of developing with a developer,

d) a step of transferring developed images onto a receiving member,

e) a step of cleaning the remaining developer.

31. An electrophotographic process according to Claim 30, wherein the charge generation layer contains pigment particles ranging in size from 0.02 μ to 0.5 μ in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

32. An electrophotographic process which comprises:

a) a step of charging an electrophotographic photosensitive member having a photosensitive layer or layers on an electroconductive substrate, said photosensitive layer comprising pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,

b) a step of exposing the charged electrophotographic photosensitive member,

c) a step of developing with a developer.

33. An electrophotographic process according to Claim 32, wherein the photosensitive layer contains pigment particles ranging in size from 0.02 μ to 0.5 μ in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

34. An electrophotographic process which comprises carrying out the following steps a), b), c), d) and e) at least twice:

a) a step of charging an electrophotographic photosensitive member having a photosensitive layer or layers on an electroconductive substrate, said photosensitive layer containing pigment particles of 0.5 μ or below in size in an amount of 80% or more in weight or number, and the particles in said size distribution being dispersed in an organic binder resin,

b) a step of exposing the charged electrophotographic photosensitive member,

c) a step of developing with a developer,

d) a step of transferring the developed images onto a receiving member,

e) a step of cleaning the remaining developer.

35. An electrophotographic process according to Claim 34, wherein the photosensitive layer contains pigment particles ranging in size from 0.02 μ to 0.5 μ in an amount of 80% or more in weight or number, and the particles of said size distribution are dispersed in an organic binder resin.

36. A process according to any of Claims 24 to 35 wherein the charge transport layer is as specified in any of Claims 3 to 23.

37. An electrophotographic photosensitive member substantially as described herein with reference to any one of the Examples.

38. A process according to Claim 24 substantially as described herein with reference to any one of the Examples.

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(54) METHOD OF PRODUCING RESIN-CONTAINING PIGMENT PREPARATIONS

(71) We, KEMISK VAERK KOGE A/S, a Danish Company of 39, Overgaden neden Vandet, Copenhagen, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of a particulate organic pigment preparation which comprises particles of a resin and an organic pigment, the pigment being dispersed within the resin particles. Such preparations need to be readily dispersible and are of value for the production of paints, varnishes, printing inks, plastics and plastic-wares.

Various ways of producing organic pigment preparations of this general type are known but the methods are often not very convenient to operate and the resulting pigment preparation often does not have as satisfactory pigmenting properties as would be desired. A particular problem is that the existing methods do not allow the production of preparations containing a large amount of pigment dispersed through the particles.

One known method for the production of pigment-resin compositions comprises working pigment into a resin softened by heating using a powerful mechanical treatment, and thereby forming pigment chips. Another method comprises milling the pigment in the presence of water and an organic solvent that is miscible with water. If desired a small amount of a water immiscible organic solvent for the resin can be present. Such a method is described in Specification No. 768,844 from which it is apparent that a combination of water, water miscible solvent and water immiscible solvent results in the formation of a liquid phase containing all three liquids.

According to the invention we make a particulate pigment preparation comprising particles of a resin and organic pigment dispersed within the resin particles, the pigment being present in the particles in an amount of 70% or more by weight based on the total weight of resin and pigment.

A method according to the invention of forming particles of resin having organic pigment uniformly dispersed therein comprises mixing the resin in particulate form, organic pigment in an amount of 70% or more by weight based on the total weight of resin and pigment, water and an organic liquid, or organic liquid mixture, that is immiscible with water and is incapable of dissolving the resin but which is absorbed in the resin and thereby forms an organic solid phase comprising the resin, pigment and organic liquid or liquids and an aqueous phase that is substantially free of organic liquid, and separating the aqueous phase from the solid phase.

By this method pigment preparations in which the particles contain 70% or more of the pigment, for example 75 to 80% or more, are obtained. Another advantage is that the mechanical treatment necessary for mixing does not have to be more than has been required in previous processes and in fact can usually be a less powerful mechanical treatment or can be conducted for a shorter time. Another advantage is that a much smaller proportion of organic liquid is needed than has been needed previously. Another advantage is that in many cases the preparation obtained on drying the solid phase is in a powdery form while in other cases it is obtained in the form of grains or lenses. These can easily be ground to powder or may be useable without grinding.

It will be appreciated that in the method of the invention the organic liquid or liquids are immiscible with water and there is no, or insignificant, dissolution of organic liquid in

the water. In the prior method there has always been a large amount of water miscible solvent, for example acetone so that the aqueous phase is an aqueous organic solvent phase in equilibrium with a resin-containing phase which also contains water and organic solvent.

In the invention the water is present solely for the purpose of facilitating the mixing process and for ensuring that discrete particles are obtained.

The resin, pigment, water and organic liquid are usually mixed together by first mixing the pigment with water and then adding the resin and organic liquid. Suitable methods of mixing the composition involve milling processes using for instance a ball mill, a vibrator mill or an attritor or by using rapidly rotating stirrers, for instance those of Cowles, Greaves or the "Kady" mill ("Kady" being a Trade Mark) or using a colloid mill. By way of example, the method may be carried out by introducing in a ball mill suitable grinding bodies, such as spheres, and dry pigment or an aqueous pigment paste together with an amount of water sufficient to secure that an easily flowing paste is formed in the mill. The ball mill is then closed and allowed to run for a short time, say half an hour to one hour, in order to homogenize the mixture. Then an organic liquid suitable for the resin to be used is introduced and the mixture is again homogenized. After homogenization, finely pulverized resin is added and the mill is rotated for a suitable number of hours. During the milling process the pigment, the resin and the organic liquid separate from the water to form a phase varying as to its form from a crystalline powder to granules or lenticular plates freely movable in the water phase. The whole mass can be washed out from the ball mill with water, whereby after filtration a water wetted product consisting of pigment, resin and organic liquid is obtained. After evaporation of adhering water and organic liquid the pigment preparation consisting of finely dispersed pigment incapsulated in resin is obtained. The preparation thus obtained may be ground to powder if desired.

Another way of mixing involves the use of a rapidly rotating stirrer and in this an aqueous pigment paste and, when necessary, an appropriate further amount of water are placed in a vessel after which the mass is homogenized and dispersed by means of the rapidly rotating stirrer. Usually a dispersing agent suitable for the pigment in question is added, this being of a kind the dispersing effect of which can be broken at a later stage of the process. Then pulverized resin is added and stirring is continued for half an hour to one hour. If a dispersing agent has been added the effect thereof is then broken and a suitable organic liquid is added. As a result the pigment, the resin and the organic liquid gather to form small grains and a water phase separates in which the grains are freely movable. After continuing the stirring for still another quarter of an hour to half an hour the particles of pigment-resin, the organic liquid contained therein as well as any excess of organic liquid and adhering water are removed from the filter residue by evaporation. After crushing, if necessary, the desired pigment preparation has been obtained.

By reason of the short time of treatment the production by means of rapidly rotating stirrers offers the possibility of obtaining a greater production capacity than when using a ball mill.

The choice of organic liquid or liquids is important. It is necessary that in the method the resin does not dissolve in the liquid, i.e. a solution of resin in liquid is not formed. However the liquid must be one that is capable of being absorbed by the resin. Thus it can be considered as becoming dissolved in the resin. This must of course be contrasted to the situation when the resin is dissolved in the liquid. Dissolution, or absorption, of the liquid in the resin involves the liquid being absorbed into the structure of the resin without destroying this structure. Swelling of the resin will normally accompany this absorption.

The applicability of a given liquid or liquid mixture for use with a particular resin can be ascertained by pouring an amount of the liquid or liquid mixture upon the resin while it is in particulate condition. If the liquid or mixture is suitable for use in the invention it will be absorbed by the resin to produce a product which, on rolling between the fingers, has low coherence, i.e. it substantially maintains its particulate nature, and which is generally transparent. If a surplus of the liquid is used then a two phase system will form, the liquid phase consisting of the liquid that has been added.

Although this appears a simple criterion for the selection of a suitable liquid or liquid mixture in practice the selection can be more difficult, for example when a pigment preparation is being prepared using widely different resins. It is therefore convenient to select the organic liquid or liquids according to particular physical data that are obtainable for the liquid or liquids and for the resin. Thus use is made of the known "solubility parameter value" of a possible liquid or mixture of liquids, combined with the knowledge of the "solubility parameter interval" of the resin under consideration. These terms are known terms and are discussed by, for example, H. Burrell in Official Digest 1955, 27, No. 369, page 726, P. Sorensen in Journal of Oil and Colour

Chemists Association 1967, volume 50, No. 3, page 226 and C. M. Hansen in "The Three Dimensional Solubility Parameter" Danish Technical Press 1967. The solubility parameter value of the liquid or liquids is a numerical constant having the dimensions $cal^{1/2} \times cm^{3/2}$. The value can be calculated on the basis of the physical properties of the liquid.

Suitable organic liquid or liquid mixtures for use in the invention are those in which the solubility parameter of the liquid or mixture has a value substantially immediately above or substantially immediately below the solubility parameter interval of the resin under consideration.

The solubility parameter intervals of resins cannot be calculated because such substances are mixtures of a number of different molecular species with different molecular weight, said species being partially unknown. They must be determined experimentally with respect to each kind of solvent. For this purpose solvents are divided in the following three groups:

Group I comprising weakly hydrogen-bonded solvents such as aliphatic or aromatic hydrocarbons which may be chlorinated or nitrated,

group II comprising moderately hydrogen-bonded solvents such as ethers, esters and ketones and

group III comprising strongly hydrogen-bonded solvents such as alcohols, amines and acids.

The solubility parameter value intervals of resins are generally published by the manufacturer or can be experimentally determined. The values are usually subject to an uncertainty of 0.4 delta units.

In the case of solvents where the solubility parameter can be calculated the solubility parameter value of a mixture of two or more liquids belonging to the same group can be calculated by simple proportionating. Some examples illustrates the method.

Ethyl cellulose has with respect to solvents of group I the solubility parameter interval 8.1.-11.1. The liquids petrol 100/140 and xylene have the solubility parameter values 7.6 and 8.8, respectively, which means that xylene dissolves in ethyl cellulose whereas petrol does not. From 85 g of the said petrol and 60 g xylene a mixture can, however, be produced of which the parameter value is $(85 \times 7.6 + 60 \times 8.8) : (60 + 85) = 8.1$ which mixture is suitable for use in connection with ethyl cellulose. If the liquids belong to different groups the useful ratio must be estimated.

Another example is a resin "vinylit VYHH" which, according to the information of the manufacturers, has a solubility parameter value interval of 9.3-11.1 with respect to solvents of group I, and 7.8-13.3 with respect to solvents of group II. The group I—solvent xylene has the solubility parameter value 8.8, whereas the group II—liquid methylbutyl ketone has a value 8.4. The latter solvent dissolves vinylit VYHH whereas xylene does not. Since xylene is placed 0.5 delta units below the solubility parameter value interval of vinylit VYHH with respect to group I and since methyl-isobutyl ketone is placed .68-units above the lower limit of the interval with respect to group II it is estimated that 6 parts of xylene and 5 parts of methyl-isobutyl ketone will constitute the correct mixture. Also a mixture consisting of equal parts of the two solvents is suitable. With benzene the same result could have been obtained but the above named mixture is preferable from a practical point of view because of the low flash-point of benzene which makes the use of this hydro-carbon difficult. Even other circumstances may influence the choice of solvents. Thus in the case of pigmented varnishes it is unsatisfactory to use liquids belonging to the groups II and III which would depreciate the lacquer.

By way of example of applications of the pigment preparations produced according to the present invention may be mentioned that copolymers of vinyl chloride and vinyl acetate are suitable as binders in paints and printing inks for gravure for which reason pigment preparations containing such copolymers are suitable for colouring such paints and printing inks, considerably improved results being obtained compared to conventional grinding of the pure pigments with a solution of the binding agent. Thus the coloured coating obtained is considerably more glossy and transparent. The pigment preparations containing ethyl cellulose are well suited for colouring nitro-cellulose varnishes and printing inks, calcium-zinc resinate printing inks, and varnishes and printing inks in which ethyl cellulose is used as a binding agent. Pigment preparations containing alcoholsoluble nitrocellulose are well suited for colouring, for instance, such compositions as alcohol soluble nitrocellulose printing inks. Pigment preparations containing cellulose acetate butyrate are well suited for colouring acryl varnishes.

As an indication of suitable combinations of solvent and resin, when the resin is a vinyl chloride vinylacetate copolymer the organic liquid may be benzene or a mixture of xylene and methyl isobutyl ketone. When the resin is polyvinyl butyral the organic liquid may be xylene. When the resin is cellulose acetate butyrate the organic liquid may be benzene. When the resin is polyvinyl chloride the organic liquid may be dichlorobenzene. When the resin is ethyl cellulose the organic liquid may be a mixture of xylene with

benzene or a mixture of xylene with petrol 100/140°C.

The provision of pigment compositions having such high organic pigment contents as 70% increases the possibility of varying the composition of the final product such as a paint, varnish, printing ink or coloured plastic since a given final pigment content can be maintained even when a greater addition of binding agents or additives are required. When producing pigmented paints, varnishes, printing inks, plastics or plastic-wares the resin-containing pigment preparation produced according to the present invention is dispersed in ground condition or without previous grinding in the binding agent in question or in one or more of the components thereof (in which latter case the manufacture of the pigmented product must later on be completed by addition of the components failing). If the pigment preparation is used in ground form a grain interval of 20-500 μ is in many cases sufficient which can be obtained easily and cheaply. If it is applied in the form of grains or in lenticular form a dimension of 3-4 mm should generally not be exceeded.

Pigmented paints, varnishes, printing inks and plastics produced by this method permit a far better utilization of the pigments than corresponding products pigmented by means of dry pigments. Thus the colour is brighter and has no grainy structure. This difference is recognizable even if the dispersion process used in the production (thereby using a pigment preparation produced according to the invention) has been fulfilled within not more than 15 minutes by stirring with a rapidly rotating stirrer. Comparable dry pigment powders must be dispersed in the same dispersing agent by a process consisting in grinding for two days in a ball mill.

In the following the invention will be illustrated by means of a number of examples.

Example 1

Into a 5 liter ball mill are introduced 1000 g of phthalocyanine blue filtercake, 30% β - copper - phthalocyanine (C.I.Pigment Blue 15), 800 g of water and 7000 g of steel balls (1.7 cm in diameter). The ball mill is closed and agitated for half an hour after which 40 g of xylene are added and the agitation is continued for one further hour whereafter 100 g "Mowital" B 30 H (a powdery polyvinylbutyral produced by Hoechst) are added. "Mowital" is a trade mark.

The ball mill is now agitated for further 16-20 hours, after which it is washed out with water and the product is isolated by filtration and dried.

There is obtained 395 g of pigment preparation in the form of glossy shells having a diameter of about 1 mm. In the example crystallisation - stabilized α-copper-phthalocyanine may be substituted for the same amount of β - copper - phthalocyanine if at the same time the proportion of xylene is increased from 40 to 50 grammes.

Example 2

Into a 5 liter ball mill are introduced 300 g of phthalocyanine green (C.I.Pigment Green 7), 1500 g of water, 100 g of "Mowital" B 30 T and 7000 g of steel balls (diameter: 1.7 cm) after which the ball mill is closed and agitated for 6 hours. Then 100 g of xylene are added and the ball mill is agitated for 16 hours after which it is washed out with water and the product is removed by filtration and dried. There is obtained 395 g of a dark powder consisting of 75% pigment and 25% polyvinylbutyral.

Example 3

Into a 5 liter ball mill are introduced 300 g of Lithol ruby (C.I.Pigment Red 57/Ca), 1500 g of water, 75 g of xylene and 1500 g steel balls (diameter: 1.7 cm). The ball mill is agitated for 1-2 hours after which 100 g of "Mowital" B 30 H are added. After further agitation of the ball mill for 16-20 hours the product is removed by flushing and separated by filtration and dried. There is obtained 395 g of lenticular shells having a diameter of 2-3 mm. These shells, consisting of 75% pigment and 25% polyvinylbutyral, are easily pulverised. In this example lack red C (C.I.Pigment Red 53/Ba) or a Lithol red 2BM (C.I.Pigment Red 48/Mn) may be substituted for Lithol ruby.

Example 4

Into a 5 liter ball mill are introduced 300 g of Benzidine yellow G.R. (C.I.Pigment Yellow 13), 1500 g of water, 100 g of "Pioloform" BL 18 (a trade mark for a polyvinylbutyral resin sold by Wacker Chernie) and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 1-2 hours after which 60 g of xylene are added and the mill agitated for 16-20 hours. The product obtained is removed by flushing with water and separated by filtration and dried. There is obtained 395 g of lenticular shells, diameter 1/2-1 mm.

Example 5

Into a 5 liter ball mill are introduced 300 g of carbon black (C.I.Pigment Black 7), 1600 g of water, 100 g of "Mowital" B 30 H and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 1-2 hours after which 100 g of xylene are added and agitated for 16-20 hours. The resulting product is washed out from the mill with water, removed by filtration and dried. There is obtained 395 g of pigment preparation in the form of glossy grains (1/2 mm) consisting

of 75% pigment and 25% "Mowital" B 30 H.

Example 6

Into a 5 liter ball mill are introduced 450 g of phthalocyanine blue (β-copper phthalocyanine) (C.I.Pigment Blue 15), 1450 g of water and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 1 hour after which 75 g of xylene and 75 g of methyl isobutyl ketone are added. Grinding is continued for 1 hour after which 150 g of vinylit VYHH (a powdery Copolymerisate of vinylchloride and vinylacetate produced by Union Carbide and Carbon Corporation) are added. The ball mill is now agitated for 16-20 hours after which the resulting product is removed by washing with water, isolated by filtration and dried. There is obtained 594 g of a dark powder consisting of 75% of pigment and 25% of vinylit VYHH.

Example 7

Into a 5 liter ball mill are introduced 450 g of permanentgelb HR (C.I.Pigment Yellow 83) (a benzidine yellow produced from Hoechst), 1350 g of water, 75 g of xylene, 75 g of methyl isobutyl ketone and 7000 g of steel balls. The ball mill is closed and agitated for 1-2 hours after which 150 g of vinylit VYHH are added. Grinding is continued for 16-20 hours after which the ball mill is opened and the resulting product is removed by washing with water, filtration and drying. There is obtained 594 g of a yellow powder consisting of 75% pigment and 25% vinylit VYHH.

Example 8

Into a 5 liter ball mill are introduced 300 g of Lithol red 2 BM (C.I.Pigment Red 48/Mn), 1500 g of water, 100 g of vinylit VYHH and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 4 hours after which 150 g of benzene are added. After further agitation for 20 hours the ball mill is opened, the product is removed by washing out with water, filtration and drying. There is obtained 396 g of granules of a diameter ranging between 1/2-1 mm and consisting of 75% pigment and 25% vinylit. The granules are easily pulverized.

Example 9

Into a 5 liter ball mill are introduced 300 g of benzidine yellow GG (C.I.Pigment Yellow 17), 1500 g of water, 100 g of vinylit VYHH and 7000 g of steel balls. The ball mill is agitated for 1-2 hours after which 50 g of xylene and 50 g of methyl isobutyl ketone are added. After continued agitation for 16 hours the ball mill is opened and the resulting product is washed out with water, filtered and dried. There is obtained 396 g of glossy, coarse powder, consisting of 75% pigment and 25% vinylit. The granules are easily pulverized.

Example 10

Into a 5 liter ball mill are introduced 300 g of phthalocyanine green (C.I.Pigment Green 7), 1500 g of water, 100 g of vinylit VYHH and 7000 g of steel balls. The ball mill is closed and agitated for 2 hours after which 50 g of xylene and 50 g of methyl isobutyl ketone are added. The ball mill is then agitated for a further 16-20 hours after which the resulting product is washed out with water, filtered and dried. There is obtained 395 g of dark shells having a diameter ranging between 1 and 2 mm and consisting of 75% pigment and 25% vinylit.

Example 11

Into a 5 liter ball mill are introduced 200 g of pyrazolon orange (C.I.Pigment Orange 34), 1500 g of water, 400 g of vinylit VYHH and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 2 hours. Then 70 g of xylene and 70 g of methyl isobutyl ketone are added. The agitation of the ball mill is continued for a further 16-20 hours after which the resulting product is removed by flushing with water, filtered and dried. There is obtained 594 g of lenticular shells having a diameter of 2-3 mm and consisting of 1/3 pigment and 2/3 vinylit.

Example 12

Into a 5 liter ball mill are introduced 300 g of Carbon Black (C.I.Pigment Black 7), 1500 g of water, 65 g of xylene, 65 g of methyl isobutyl ketone and 7000 g of steel balls. The ball mill is agitated for 1-2 hours after which 300 g of vinylit VYHH are added. After a further 1 hour's milling, 25 g of methyl isobutyl ketone are added. The agitation is continued for further 16-20 hours after which the ball mill is flushed out with water and the resulting product is removed by filtration and dried. There is obtained 594 g of granules measuring 1/2-1 mm and consisting of 50% pigment and 50% resin. The granules are easily pulverized.

Example 13

Into a 5 liter ball mill are introduced 375 g of benzidine yellow GR (C.I.Pigment Yellow 13), 1500 g of water, 125 g of ethyl cellulose Nlo, in the form of powder (Hercules) and 7000 g of steel balls. The ball mill is closed and agitated for 1 hour. 85 g of petrol, 100/140°C, are added and the ball mill is further agitated for half an hour after which 50 g of xylene are added. Grinding is now continued for 16-20 hours after which the resulting product is washed out with water, filtered and dried. There is obtained 495 g of crystalline powder consisting of 75% pigment and 25% ethyl cellulose.

Example 14

Into a 5 liter ball mill are introduced 400 g of phthalocyanine blue (β-copper phthalocyanine) (C.I.Pigment Blue 15), 1700 g of water, 100 g of xylene and 7000 g of steel balls. The ball mill is closed and agitated for 1 hour. 100 g of ethyl cellulose Nlo are added. Grinding is continued for 16-20 hours after which the product produced is washed out with water, filtered and dried. 495 g of a crystalline powder consisting of 80% pigment and 20% ethyl cellulose are obtained.

Example 15

375 g of Lithol ruby (C.I.Pigment Red 57/Ca), 1550 g of water, 125 g of ethyl cellulose Nlo and 7000 g of steel balls are introduced into a 5 liter ball mill. Agitation for 1 hour, after which 120 g of petrol 100/140 are added and grinding continued for half an hour, after which 50 g of benzene are added. The ball mill is now agitated for a further 16-20 hours, after which the resulting product is washed out with water, filtered and dried. There results 495 g of a crystalline powder consisting of 75% pigment and 25% ethyl cellulose.

Example 16

300 g of phthalocyanine blue (β-copper phthalocyanine) (C.I.Pigment Blue 15), 1200 g of water, 7000 g of steel balls and 60 g benzene are introduced into a 5 liter ball mill. The mill is agitated for 1 hour, after which 100 g of cellulose acetate butyrate, having a viscosity of 1/2 sec. as measured by viscosimeter according to Eastman, are added. Agitation is now continued for 16-20 hours, after which the resulting product is removed by flushing with water, filtered and dried. There is obtained 396 g of fine shells consisting of 75% pigment and 25% of cellulose acetate butyrate.

Example 17

Into a 5 liter ball mill are introduced 300 g of phthalocyanine blue (β-copper phthalocyanine) (C.I.Pigment Blue 15), 1500 g of water, 7000 g of steel balls and 100 g of Vestolit (a polyvinyl chloride product from Hoechst). The ball mill is agitated for 2 hours, after which 100 g of dichloro benzene are added. The ball mill is agitated for 16-20 hours, after which the resulting product is flushed out from the mill with water, filtered and dried. There is obtained 396 g of a dark powder consisting of 75% pigment and 25% PVC.

Example 18

300 g of phthalocyanine blue (β-copper phthalocyanine) (C.I.Pigment Blue 15), 1500 g of water and 154 g of nitro-cellulose RF 10, 65% (ethanol wetted nitrocellulose from Bofors) are stirred up into a glass containing 3 liters by means of a rapidly rotating stirrer. While still continuing the stirring the following constituents are added in the order mentioned: 70 g of xylene, 30 g dibutylphthalate and 70 g methyl isobutyl ketone. The mixture is poured into a 5 liter ball mill and 7000 g steel balls are added, after which the ball mill is agitated for 16-20 hours. The resulting product is flushed out of the mill with water, filtered and dried. There is obtained 325 g of a dark powder consisting of 70% pigment, 23% nitrocellulose and 7% dibutylphthalate.

Example 19

187.5 g of aqueous phthalocyanine green filtercake (C.I.Pigment Green 7), 32%, are stirred in a Greave's mixer with a solution of 6 g diamine BG (Liljeholmens Stearinfabrik AB), and 3 g glacial acetic in 50 g water. Stirring is continued for 20 minutes. Then 90 G vinylit VYHH are added and stirring is intensified for 20 minutes. While continuing the stirring 40 g xylene and 40 g methyl isobutyl ketone are added and stirring is continued for further 20 minutes. 25 ml sodium hydroxide solution, 2N, are added in the course of 5 minutes, after which stirring is continued for further 20 minutes. The product resulting is removed by filtration, washed and dried. There is obtained 152 g of a dark powder consisting of about 39% pigment and about 38.5% vinyl.

Example 20

55.5 kg phthalocyanine blue filter cake, 36% (β-copper phthalocyanine) (C.I.Pigment Blue 15), 100 kg water and 1 kg aerosol TR (a dispersing agent produced by Hardman & Holden) are stirred by means of a rapidly rotating agitator (Greaves). 30 kg vinylit VAGH are added and agitation continued for 20 minutes. While still continuing agitation a mixture of 0.44 kg sulphuric acid, 98%, and 2 kg water are added in the course of 5 minutes, after which agitation is continued for a further 20 minutes. While stirring is still continued a mixture of 13 kg xylene and 13 kg methyl isobutyl ketone are added in the course of 10 minutes, after which stirring is continued for further 30 minutes. The resulting powder is filtered, washed and dried. There is obtained 44 kg powder consisting of 40% pigment and 60% vinylit.

Example 21

975 g Permanentgelb HR-filtercake, 27.7% (C.I.Pigment Yellow 83) and 325 g water are stirred in a Greave's mixer. 90 g vinylit VYHH are added and stirring is continued for 20 minutes. While the stirring is still continued a mixture of 60 g xylene and 60 g methyl isobutyl ketone are added, and stirring continued for further 50 minutes. The resulting product is filtered, washed

and dried. There is obtained 354 g powder consisting of 75% pigment and 25% vinylit.

Example 22

120 g carbon black (C.I.Pigment Black 7) and a mixture of 90 g xylene and 90 g methyl isobutyl ketone are added by means of a spatula and the mixture is left in a dissolver container (Cowles) for 24 hours with the cover closed. 1000 g water are added. The mixture is stirred with Cowles dissolver for 5 minutes, after which 180 g vinylit VYHH powder are added in the course of 5-10 minutes, while still stirring, the stirring being continued for a further 30 minutes. The resulting product is filtered, washed and dried. There is obtained 297 g black powder consisting of 40% pigment and 60% vinylit.

Example 23

283 g aqueous benzidine yellow GG filtercake, 21.2% (C.I.Pigment Yellow 17) and a solution of 6 g fat amine OL and 3 g glacial acetic acid and 11o g water are stirred in a Greaves mixer. 120 g vinylit VYHH are added, after which agitation is continued for 20 minutes. While still stirring a mixture of 50 g water and 20 ml sodium hydroxide solution, 2M, added after which agitation is continued for 20 minutes. While still agitating, a mixture of 35 g xylene and 35 g methyl isobutyl ketone are added and stirring is continued for 20 minutes. The resulting product is filtered, washed and dried. There is obtained 180 g yellow powder consisting of about 32% pigment and about 65% vinylit.

Example 24

253 g aqueous permanent carmine FBB, extra in the form of a filter cake containing 23.7% pigment (C.I.Pigment Red 146), 250 g of water and 120 g of vinylit VYHH are stirred in a Greaves mixer and stirring continued for 20 minutes, after which a mixture of 46 g xylene and 46 g methyl isobutyl ketone are added in the course of 5-10 minutes with continued stirring, which thereafter is further continued for 30 minutes. The resulting product is filtered and dried. There is obtained 178 g red powder consisting of 33 1/3% pigment and 66 2/3% vinylit.

Example 25

338 g aqueous benzidine yellow GR, filter cake (C.I.Pigment Yellow 13), 26.6%, and a solution of 9 g fat amine OL and 4 1/2 g glacial acetic acid in 170 g water are stirred in a Greaves mixer, after which 90 g ethyl cellulose Nlo are added and stirring continued for 20 minutes. While stirring is still continued 9 g ammonia, 25%, and 250 g water are added in the course of about 5 minutes, after which stirring is continued for 20 minutes. Now on further stirring 59 g petrol 110/140 are added, followed by 41 g xylene, after which stirring is continued for 30 minutes. The product resulting is filtered, washed and dried, whereby 185 g yellow powder consisting of about 48.5% ethyl cellulose and 48.5% pigment is obtained.

Example 26

278 g aqueous phthalocyanine blue filter cake (β-copper phthalocyanine) (C.I.Pigment Blue 15), 5 g aerosole TE and 500 g water are stirred in a Greaves mixer, 100 g Mowital B 30 H are added and stirring is contined for 20 minutes. While the stirring is still continued 11 ml sulphuric acid, 2M, are added and stirring is continued for 20 minutes. Now under agitation 110 g xylene are added within 5 minutes and stirring continued for 30 minutes. The product resulting is filtered, washed and dried. There is obtained 198 g dark powder consisting of 50% pigment and 50% polyvinylbutyral.

Example 27

In a 1250 liter ball mill there are introduced 120 kg steel balls (1.7 cm in diameter), 75 kg phthalocyanine blue (C.I. Pigment Blue 15) and 100 kg water. The ball mill is closed and agitated for 1 hour. After this 275 kg water are added and agitation is continued for half an hour. 8 kg xylene is added, agitation continued for 1 hour and 25 kg "Mowital" B 30 H are added. The ball mill is now agitated for 16 hours at 20-30°C, after which the resulting product is washed out of the mill, filtered, washed cautiously and dried. After drying 98 kg lenticular plates, 1/2-1 mm in diameter and consisting of 75% pigment and 25% polyvinylbutyral are obtained.

Example 28

In a 5 liter ball mill the following components are introduced: 300 g benzidine yellow G (C.I.Pigment Yellow 12), 1500 g water, 40 g petrol 100/140°C, and 7000 g steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 2 hours, after which 100 g "Pentalyn" K (a trade mark for a maleinate resin from Hercules Company) are added. Milling is continued for 16 hours, after which the resulting product is washed out with water, filtered and dried. There is obtained 197 g of a crystalline powder consisting of 75% pigment and 25% maleinate resin.

Example 29

Production of nitro cellulose printing ink based on spirits

29 g A
29 g B
8,9 g dibutyl phthalate
16,3 g isopropyl acetate
7,5 g butyl acetate
5 g ethanol

are weighed out in a 250 ml tin suitable for using connection with a small rapidly rotating stirrer. Under agitation 13.3 g pigment preparation produced according to example 2 and containing 10 g pigment (Phthalocyanine green) is added. In the above prescription the designations A, B refer to a solution of nitro cellulose and a mixture of equal parts of Arochem and ethanol, respectively.

Intensive agitation is continued for 15 minutes, after which ethanol is added for the purpose of dilution until the viscosity is 25-30 seconds measured on the DIN-cup No. 4, has been attained, which requires about 43 g of ethanol.

For the purpose of comparison with the printing ink thus produced another printing ink having the same proportion of the same pigment is produced by using the pigment in the form of powder. This is accomplished by introducing the following constituents in a ball mill:

10 g phthalocyanine green
40 g A
20 g B
8 g dibutyl phthalate
15 g isopropyl acetate
7 g buytl acetate
300 g ceramic balls

after which the ball mill is activated and remained agitated for 48 hours. Then the milled product is diluted with ethanol in the same manner as above described to obtain the viscosity of 25-30 seconds made on DIN-cup No. 4.

When the two printing inks are printed adjacent to each other on various materials such as aluminium foil, cellophane and paper, it will be found that the former is considerably more glossy and transparent than the latter.

WHAT WE CLAIM IS:—

1. A particulate pigment preparation comprising particles of a resin and organic pigment dispersed within the resin particles, the pigment being present in the particles in an amount of 70% or more by weight based on the total weight of resin and pigment.

2. A methid of producing particles of resin having organic pigment dispersed within the particles, the pigment being present in the particles in an amount of 70% or more by weight based on the total weight of resin and pigment, comprising mixing together the resin in particulate form, organic pigment in an amount of 70% or more by weight based on the total weight of resin and pigment, water and an organic liquid, or organic liquid mixture, that is immiscible with water and is incapable of dissolving the resin but which is absorbed in the resin, and thereby forming an organic solid phase comprising the resin, pigment and organic liquid or liquids, and an aqueous phase that is substantially free of organic liquid, and separating the aqueous phase from the solid phase.

3. A method according to claim 2 comprising the additional step of removing the organic solvent from the solid phase.

4. A method according to claim 2 or claim 3 in which the organic liquid or organic liquid mixture is one which has a solubility parameter value substantially immediately above or substantially immediately below the solubility parameter interval of the resin.

5. A method according to any of claims 2 to 4 in which the resin is a vinyl chloride vinyl acetate copolymer and the solvent is benzene or a xylene-methyl isobutyl ketone mixture.

6. A method according to any of claims 2 to 4 in which the resin is polyvinyl butyral and the organic liquid is xylene.

7. A method according to any of claims 2 to 4 in which the resin is cellulose acetate butyrate and the organic liquid is benzene.

8. A method according to any of claims 2 to 4 in which the resin is polyvinyl chloride and the organic liquid is dichloro benzene.

9. A method according to any of claims 2 to 4 in which the resin is ethyl cellulose and the organic liquid is a mixture of xylene with petrol 100/140°C or xylene with benzene.

10. A method according to any of claims 2 to 9 in which the mixing is conducted by ball milling.

11. A method according to any of claims 2 to 9 in which the mixing is conducted by stirring with a rotating stirrer.

12. A method according to any of claims 2 to 11 in which the water is first added to the pigment and the organic liquid and resin are added subsequently.

13. A method according to claim 2 substantially as herein described with reference to any of the Examples.

14. A particulate pigment preparation comprising particles of a resin and pigment dispersed within the resin particles obtained by a method according to any of claims 2 to 13.

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